

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-203576

(43)Date of publication of application : 19.07.2002

(51)Int.Cl.

H01M 8/02

H01M 4/86

H01M 4/88

H01M 8/10

(21)Application number : 2000-401274

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(22)Date of filing : 28.12.2000

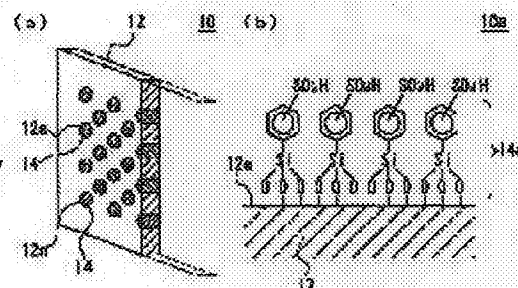
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(54) ELECTROLYTE FILM AND FUEL CELL USING THIS

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an electrolyte film which can obtain high ion conductivity by introducing relatively little amount of ion exchange group, and to raise CO-resistant nature of an electrode and its durability, by mitigating or making needless to humidify the electrolyte by accessory machine, in a low-temperature operating type fuel cell.

SOLUTION: The electrolyte film 10 is provided with a film support body 12 which has a through hole 12a penetrating in a thickness direction, and an ion conductive substance 14 introduced into the inside of the through hole 12a. Moreover, the fuel cell has a film electrode zygote 20 which joins an anode 40a and a cathode 40b to both sides of the electrolyte film 30 having the structure such as the above descriptions. Moreover, the anode 40a and the cathode 40b are provided with catalyst layers 44a and 44b which gaseous phase side surfaces of the electrolytes 50a and 50b in the catalyst layer are covered with water repellant layers 52a and 52b. It is desirable to use a fluoride system material as the water repellant 52a and 52b.



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DETAILED DESCRIPTION

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## [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the electrolyte membrane used for a fuel cell and this suitable as a portability type small power supply, the source of power for mount, a cogeneration system, etc. in more detail about the fuel cell which used an electrolyte membrane and this.

[0002]

[Description of the Prior Art] A fuel cell is classified into a solid polymer type, a phosphoric acid type, an alkali type, a melting carbonate type, a solid oxide type, etc. according to the kind of electrolyte to be used. Since there are few restrictions in a low temperature operation type fuel cell and the material face where especially a polymer electrolyte fuel cell constitutes a fuel cell and the miniaturization and the weight saving are possible in these, the application to portability type a small power supply, the source of power for mount, etc. is expected. However, in order to apply a polymer electrolyte fuel cell especially as the mounted source of power, to attain a high increase in power and a miniaturization further is desired.

The issue which should be solved for that purpose is left behind.

[0003] The 1st technical problem occurs by a raise in ion conduction and high-intensity-izing of an electrolyte membrane. In the case of a polymer electrolyte fuel cell, it is common to use as an electrolyte poly membranes represented by Nafion (a registered trademark, the Du Pont make), such as a perfluoro system electrolyte, various hydrocarbon system electrolytes, etc. not constructing a bridge. In order to make such a polymer electrolyte fuel cell high-powered, the higher one of the ionic conductivity of a poly membrane is desirable. Since a fuel cell is generally used as a stack which laminated many cells, in order to miniaturize a polymer electrolyte fuel cell, the thinner one of the thickness of a poly membrane is preferred, and, for that purpose, its higher one is [ the intensity of a poly membrane ] desirable.

[0004] However, since it is generally random in distribution of the ion exchange group in a poly membrane, in the place where the density of an ion exchange group is low, resistance becomes large. Therefore, high ionic conductivity is not obtained in a poly membrane with low ion exchange group density. On the other hand, if ion exchange group density is made high, the ionic conductivity of a poly membrane will become high. However, when the ion exchange group density of a poly membrane becomes high, a film serves as water solubility in a certain place, and there is a problem that the intensity of a poly membrane falls. That is, it is

difficult to reconcile high ionic conductivity and high intensity in a poly membrane.

[0005]In the conventional polymer electrolyte fuel cell, it is common to use the method of raising ion exchange group density, maintaining the intensity of a poly membrane according to composite-izing or bridge construction, in order to solve this problem. For example, to JP,10-312815,A. In order to improve the dimensional stability and handling \*\*\*\* of a perfluoro system electrolyte, the bipolar membrane which impregnated with the ion-conductive polymer (for example, perfluoro sulfonic acid) the porous support (for example, nonwoven glass fiber) in which textiles carried out orientation at random is indicated.

[0006]The 2nd technical problem occurs by the formation of a dry-proof rise of an electrolyte membrane, and flooding-proof-ization of an electrode. As an electrolyte membrane used for a polymer electrolyte fuel cell, although various materials are known, each of these needs water for revealing ion conductivity. Therefore, if the operating condition of a fuel cell turns into dry conditions, it will become a cause by which the water content of an electrolyte membrane falls and ionic conductivity falls and by which what is called a dry rise occurs and the output of a fuel cell is reduced.

[0007]In the conventional polymer electrolyte fuel cell, in order to solve this problem, it is common to use the method of using auxiliary machinery and supplying moisture to an electrolyte membrane from the exterior. The method of specifically humidifying reactant gas to an electrolyte membrane, using Vavra, a mist generator, etc. as a method of supplying moisture, the method of pouring moisture into the reactant gas channel formed in the inside of a separator directly, etc. are known.

[0008]Generally, a polymer electrolyte fuel cell joins the electrode of a couple to both sides of solid polyelectrolyte membrane, and makes it a membrane electrode zygote, and the structure which sandwiched the both sides with the separator is taken. Since it is necessary to secure in an electrode the three-phase zone with which the three phase of an electrolyte, a catalyst, and reactant gas coexists in order to advance a cell reaction, generally the electrode has porous structure containing a catalyst and an electrolyte.

[0009]On the other hand, in the case of a polymer electrolyte fuel cell, in a cathode, water generates by a cell reaction. When a proton moves to the cathode side from the anode side, water also moves to the cathode side by electroendosmose. Therefore, if the operating condition of a fuel cell turns into wet conditions, especially in a cathode, superfluous water will stagnate easily. If this water is neglected, it will become a cause by which the fine pores in an electrode blockade with water, and supply of reactant gas is checked and by which it is generated by what is called flooding and the output of a fuel cell is reduced.

[0010]In the conventional polymer electrolyte fuel cell, in order to solve this problem, it is common to use the method of optimizing electrode structure. For example, in order to increase a three-phase zone, the method of making an electrode a diffusion zone and the two-layer structure of a catalyst bed provided in the field which touches solid polyelectrolyte membrane is known. A diffusion zone is a layer for performing supply of the reactant gas to a catalyst bed, and electronic transfer.

Generally, the material which has porosity and electron conductivity is used.

A catalyst bed is a layer used as the reaction field of a cell reaction.

Generally, it consists of a catalyst which the catalyst or the carrier was made to support, and an electrolyte (electrolyte in a catalyst bed) which has the same ingredient as solid polyelectrolyte membrane.

[0011]For example, in order to increase a reaction site to an electrode, the porous electrode to which the

catalyst support carbon by which the surface was covered with the solid polymer electrolyte was made to bind with fluororesin is indicated by JP,5-36418,A.

[0012]To JP,9-320611,A. In order to give water repellence uniformly to a porous electrode, the electrode for polymer electrolyte fuel cells produced by applying to solid polyelectrolyte membrane the mixed liquor of a solvent soluble fluorine polymer which does not have carbon black, fluorine system ion-exchange resin, and the ion exchange group which supported the platinum catalyst is indicated. It is considered as a porosity film by kneading and extending the mixture of the carbon black which supported the platinum catalyst in the gazette, and polytetrafluoroethylene, The electrode for polymer electrolyte fuel cells produced by impregnating this with the solvent soluble fluorine polymer which does not have fluorine system ion-exchange resin and an ion exchange group is indicated.

[0013]The 3rd technical problem occurs by CO-proof-ization of an electrode. Although pure water matter can also be used for the fuel gas of a polymer electrolyte fuel cell, using the reformed gas obtained by carrying out steam reforming of the hydrocarbon is also examined. However, a little CO gas may be contained in this reformed gas. Although the catalyst of a platinum system is generally used for the electrode of a polymer electrolyte fuel cell, in a low temperature region, even if especially platinum is a little COs, poisoning of it is carried out, and it causes loss of power.

[0014]In the conventional polymer electrolyte fuel cell, in order to solve this problem, it is common to use CO-proof nature catalyst. Specifically as a CO-proof nature catalyst, the alloy catalyst of a platinum system which added a ruthenium, iridium, rhodium, etc. is known to platinum.

[0015]

[Problem(s) to be Solved by the Invention]The following problems are among the conventional technologies mentioned above. Since orientation of the stoma inside porous support is carried out at random when using the bipolar membrane which impregnated with the ion-conductive polymer the porous support in which textiles carried out [ 1st ] orientation at random as an electrolyte membrane, it is a part of them which is contributed effective in ion conduction among the introduced ion exchange groups. Therefore, in order to obtain high ionic conductivity, it is necessary to introduce a lot of ion-conductive polymers into porous support. However, in order to maintain the intensity of bipolar membrane, the porosity of porous support can seldom be enlarged. Therefore, a limit is among high ion conduction-ization which used such bipolar membrane.

[0016]When humidifying [ 2nd ] an electrolyte using auxiliary machinery, various components, such as a condenser for collecting the water discharged from the water tank for storing the water for humidification, a humidifier, and a fuel cell, are needed. Therefore, there is a problem that the whole fuel cell system is complicated, and is enlarged. Excessive auxiliary machine power is needed and humidification of the electrolyte using auxiliary machinery also becomes the cause of reducing the generation efficiency of a fuel cell.

[0017]On the other hand, in the case of a polymer electrolyte fuel cell, as mentioned above, to the cathode side, water generates by a cell reaction. humidification of the electrolyte by auxiliary machinery if this produced water can be directly used for electrolytic humidification -- mitigation -- or it can become unnecessary and the miniaturization of the whole fuel cell system, a weight saving, and efficient-ization can be expected.



[0018]However, the conventional electrode used for a polymer electrolyte fuel cell does not have structure by which the thing which made easy to discharge the water which stagnates in an electrode, such as giving a water-repellent finish at the fine-pores internal surface of an electrode, is common, and was suitable for effective use of produced water, in order to control the loss of power by flooding.

[0019]For example, the electrode for polymer electrolyte fuel cells indicated by JP,9-320611,A covers at least a part of fine-pores internal surface of an electrode with the solvent soluble fluorine polymer which does not have an ion exchange group, and is aiming to give water repellence. However, it is difficult to cover thinly with a solvent soluble fluorine polymer uniformly all the ion exchange groups exposed to a gaseous phase side surface using the indicated method. Therefore, in order the great portion of produced water by a cell reaction is discharged out of an electrode from the inside of fine pores, and it is not used effectively for electrolytic humidification, and to stabilize it and to operate it, its humidification by auxiliary machinery is indispensable.

[0020]In the 3rd, CO-proof nature catalyst has a function which carries out oxidation removal of CO which arrived at the catalyst surface, or prevents adsorption of CO. Degradation with the passage of time of such a function of CO-proof nature catalyst is carried out by being put to CO gas atmosphere for a long time. Therefore, there is a limit in CO-proof-ization of the electrode using CO-proof nature catalyst.

[0021]The issue which this invention tends to solve is preferred as an electrolyte membrane used for a low temperature operation type fuel cell, and there is in providing the electrolyte membrane from which high ionic conductivity is moreover relatively obtained with a little ion exchange group introduction amounts.

[0022]There are other issues which this invention tends to solve in providing mitigation or the fuel cell which becomes unnecessary and is produced by stabilizing a high output under the condition of not humidifying about humidification of the electrolyte by auxiliary machinery in a low temperature operation type fuel cell.

[0023]Other issues which this invention tends to solve are in raising the CO-proof nature of an electrode, and its endurance in a low temperature operation type fuel cell.

[0024]

[Means for Solving the Problem]An electrolyte membrane built over this invention in order to solve an aforementioned problem makes it a gist to have a film base material which has a communicating hole penetrated to a thickness direction, and an ion-conductive substance introduced into an inside of said communicating hole.

[0025]When a film base material which has a communicating hole penetrated to a thickness direction is used as porous support for introducing an ion-conductive substance, an introductory place of an ion-conductive substance is pinpointed. Therefore, even if it is when there are few introduction amounts of an ion-conductive substance, i.e., an introduction amount of an ion exchange group, relatively, high ionic conductivity is obtained.

[0026]In a fuel cell with which the 2nd of this invention was provided with a membrane electrode zygote to which an electrode was joined by both sides of an electrolyte membrane, said electrolyte membrane makes it a gist to have a film base material which has a communicating hole penetrated to a thickness direction, and an ion-conductive substance introduced into an inside of said communicating hole.

[0027]Since electrolyte membranes by which an ion-conductive substance was introduced into an inside of a communicating hole of a film base material which has a communicating hole penetrated to a thickness

direction are high ionic conductivity and high intensity relatively, if this is used as an electrolyte membrane of a low temperature operation type fuel cell, they can attain a high increase in power and a miniaturization of a fuel cell.

[0028]In this case, as for at least one side of said electrode, it is desirable to have a catalyst bed containing a catalyst supported by a catalyst or carrier and an electrolyte in a catalyst bed, and to cover a gaseous phase side surface of an electrolyte in said catalyst bed with a hydrophobic layer which has reactant gas permeability. As for said hydrophobic layer, consisting of fluorine system material is desirable.

[0029]Discharge of water from a catalyst bed to the diffusion-zone side is controlled without checking diffusion of reactant gas to a catalyst bed, if a gaseous phase side surface of an electrolyte in a catalyst bed is covered with a hydrophobic layer which has reactant gas permeability. As a result, some produced water by a cell reaction stagnates in an inside of a catalyst bed. By diffusion, moisture which stagnated in an inside of a catalyst bed is returned to an electrolyte membrane, and is reused by humidification of an electrolyte membrane. Therefore, under low humidification or a condition of not humidifying, water content of an electrolyte membrane is maintainable to the level required for a stable operation, and a high output is obtained by being stabilized.

[0030]Since transmissivity of CO is low, if this is used for a thin layer which consists of fluorine system material as a hydrophobic layer, CO poisoning of a catalyst included in a catalyst bed will be controlled. Since frequency where a catalyst contacts CO gas decreases, the endurance of an electrode also improves.

[0031]

[Embodiment of the Invention]Hereafter, it explains in detail, referring to drawings for an embodiment of the invention. The outline lineblock diagram of the electrolyte membrane concerning the 1 embodiment of this invention is shown in drawing 1. The electrolyte membrane 10 is provided with the following in drawing 1 (a).  
Film base material 12.

Ion-conductive substance 14.

[0032]The film base material 12 is provided with the communicating hole 12a of a large number penetrated to a thickness direction. Below  $30000\text{-nm}^2$  of the cross-section area of this communicating hole 12a is [ more than  $0.2\text{-nm}^2$  ] preferred. If the cross-section area of the communicating hole 12a becomes less than  $0.2\text{-nm}^2$ , since ion conduction will be barred, it is not desirable. If the cross-section area of the communicating hole 12a exceeds  $30000\text{-nm}^2$ , since the ionic conductivity of the electrolyte membrane 10 whole will fall, it is not desirable. The cross-section area of the communicating hole 12a of more than  $0.2\text{-nm}^2$  is below  $100\text{-nm}^2$  still more preferably.

[0033]Many numbers per unit area of the communicating hole 12a are so preferred that there are as long as the intensity of the film base material 12 is maintainable. In order to give high ionic conductivity to the electrolyte membrane 10, more than  $1 \times 10^9 / \text{cm}^2$  are desirable still more preferred, and the numbers per unit area of the communicating hole 12a are  $3 \times 10^{10} / \text{cm}^2$  or more than  $\text{cm}^2$ .

[0034]The communicating hole 12a is penetrated to the thickness direction of the film base material 12 at least, and the shape in particular should not just be limited. For example, the communicating hole 12a may

incline at the angle below 90 degrees to the field of the film base material 12. The communicating hole 12a may be linear shape, or may be zigzag shape. However, it is more desirable to have penetrated the communicating hole 12a almost vertically to the film base material 12, in order to make membrane resistance of the electrolyte membrane 12 into the minimum. The shape of the section of a communicating hole should just be the shape which can introduce an ion conductivity substance, and the shape in particular is not limited further again. For example, the section of the communicating hole 12a may be circular, an ellipse form may be sufficient as it, or a polygon may be sufficient as it, and the shape which can connect and do the above-mentioned figure like a gourd form or a star shape further again may be sufficient as it.

[0035]The construction material of the film base material 12 can make the above communicating holes 12a, and should not just be limited in particular. For example, it may be a polymer material or may be an inorganic material. It may be a complex of organic materials and an inorganic material.

[0036]The polycarbonate membrane etc. which the communicating hole has specifically penetrated vertically to a field as the film base material 12 with the alumina membrane, the electron beam irradiation, and the solvent which the communicating hole has penetrated vertically to a field are mentioned as a suitable example.

[0037]The ion-conductive substance 14 is introduced into the inside of communicating hole 12a of the film base material 12. The ion-conductive substance 14 should just be a substance which has an ion exchange group and can be introduced into the inside of communicating hole 12a, and is not limited in particular. As long as it can introduce, it is so good that there is much quantity of the ion conductivity substance 14 introduced into the communicating hole 12a, i.e., the quantity of an ion exchange group. in order to give high ionic conductivity to the electrolyte membrane 10 -- the quantity (this is hereafter called "ion exchange group surface density".) of the ion exchange group per unit area --  $1/\text{nm}$  -- more than  $2$  -- desirable -- further -- desirable --  $10/\text{nm}$  -- it is more than  $2$ .

[0038]It says [ "introduces the ion-conductive substance 14" in this invention ] giving ion conductivity to the inside of communicating hole 12a, or its internal surface. It is mentioned as an example with impregnating with the ion-conductive substance 14, specifically suitable embellishing the internal surface of the communicating hole 12a with the ion-conductive substance 14, etc. for the inside of the communicating hole 12a.

[0039]When impregnating the inside of communicating hole 12a with the ion-conductive substance 14, as the ion-conductive substance 14, it is preferred to use a solid polymer electrolyte. In this case, a solid polymer electrolyte is the fluorine system polymer by which all or a part of polymer skeleton was fluorinated, may be provided with the ion exchange group, is a hydrocarbon system polymer which does not contain fluoride in a polymer skeleton, and may be provided with the ion exchange group.

[0040]Also about the ion exchange group contained in these polymers, it is not limited in particular and can choose arbitrarily according to a use. That is, ion exchange groups may be any, such as sulfonic acid, carboxylic acid, phosphonic acid, and phosphonous acid. One kind of ion exchange group may be contained in these polymers, or two or more sorts of ion exchange groups may be contained in them.

[0041]As a solid polymer electrolyte in which all or a part of polymer skeleton was fluorinated, Specifically Perfluorocarbon-sulfonic-acid system polymers, such as Nafion (registered trademark), A perfluorocarbon

phosphonate system polymer, a trifluoro styrene-sulfonic-acid system polymer, an ethylene tetrafluoroethylene g-styrene-sulfonic-acid system polymer, etc. are mentioned as a suitable example.

[0042]Specifically as a solid polymer electrolyte of the hydrocarbon system which does not contain fluoride, polysulfone sulfonic acid, PORIARIRU ether ketone sulfonic acid, polybenzimidazole alkyl sulfonic acid, polybenzimidazole alkyl phosphonic acid, etc. are mentioned as a suitable example.

[0043]When it embellishes the internal surface of the communicating hole 12a with the ion-conductive substance 14, it is preferred to use the coupling agent which can introduce the coupling agent or ion exchange group which has an ion exchange group as the ion-conductive substance 14. In this case, the coupling agent to be used chooses the optimal thing according to the construction material of the film base material 12. For example, when the film base material 12 consists of a composite material containing the inorganic material of oxide stock, the organic materials which have an OH radical at the end, or these either, as the ion-conductive substance 14, a silane coupling agent, the coupling agent of a titanate system, etc. are preferred.

[0044]As a coupling agent which can introduce an ion exchange group, Specifically Phenyltrimethoxysilane, phenyltriethoxysilane, These oligomer, such as phenyltrichlorosilane, phenyldimethylchlorosilicane, phenyldimethylethoxysilane, phenethyl trichlorosilane, and 3-(N-allylamino) propyltrimethoxysilane, is mentioned as a suitable example.

[0045]When it embellishes the internal surface of the communicating hole 12a with a coupling agent, an ion exchange group may introduce an ion exchange group into a coupling agent, after embellishing the communicating hole 12a with the coupling agent which may be beforehand introduced into the coupling agent or does not contain an ion exchange group.

[0046]The kind in particular of ion exchange group introduced into a coupling agent is not limited, and can be arbitrarily chosen according to a use. That is, ion exchange groups may be any, such as sulfonic acid, carboxylic acid, phosphonic acid, and phosphonous acid. One kind of ion exchange group may be contained in these coupling agents, or two or more sorts of ion exchange groups may be contained in them.

[0047]The expanded sectional view of the electrolyte membrane 10a which used the coupling agent 14a as an ion-conductive substance is shown in drawing 1 (b). The electrolyte membrane 10a illustrated to drawing 1 (b) is embellished by the silane coupling agent 14a in which the internal surface of the communicating hole 12a which penetrates the film base material 12 has a phenyl group, and the sulfonic group is introduced into each phenyl group, respectively.

[0048]Next, an operation of the electrolyte membrane concerning this embodiment is explained. In the case of the bipolar membrane which impregnated with the ion-conductive polymer the porous support to which orientation of the textiles was carried out at random, inside porous support, orientation will be carried out the stoma at random. Therefore, even if it impregnates this with an ion-conductive polymer, the ion exchange group which contributes to ion conduction substantially is only a part of them. Therefore, in order to obtain high ionic conductivity, it is necessary to impregnate with a lot of ion-conductive polymers.

[0049]On the other hand, when using the film base material 12 which has the communicating hole 12a penetrated to a thickness direction as porous support, all the communicating holes 12a function as an ion conduction path substantially. Therefore, if the ion-conductive substance 14 is introduced into the inside of communicating hole 12a of such a film base material 12, most ion exchange groups contained in the ion-



conductive substance 14 will contribute effective in ion conduction. Therefore, even if it is when there are few introduction amounts of an ion exchange group relatively, high ionic conductivity is obtained.

[0050]Inter-electrode [ by which the communicating hole 12a is especially established in the both sides of the electrolyte membrane 10 to the field of the film base material 12 when almost vertical ] will be connected in the shortest ion migration course. Therefore, the membrane resistance of the electrolyte membrane 10 becomes small, and high ionic conductivity is obtained.

[0051]Since the ion exchange group introduced into the film base material 12 is [ the rate which contributes effective in ion conduction ] high, even if it is when the porosity of the film base material 12 is relatively small, high ionic conductivity is obtained. That is, according to the electrolyte membrane 10 concerning this invention, as compared with the conventional bipolar membrane, coexistence with high ionic conductivity and high intensity is attained.

[0052]Next, it explains in detail, referring to drawings for the fuel cell concerning this invention using the electrolyte membrane mentioned above. The expanded sectional view of the membrane electrode zygote with which the fuel cell concerning the 1 embodiment of this invention is equipped is shown in drawing 2. The membrane electrode zygote 20 is provided with the following in drawing 2.

Electrolyte membrane 30.

The anode 40a joined by the field of one of these.

The cathode 40b joined by the field of another side.

[0053]Here, the electrolyte membrane 30 consists of a thing provided with the film base material 32 which has the breakthrough 32a penetrated to a thickness direction, and the ion-conductive substance 34 introduced into the inside of breakthrough 32a. Since the detailed composition of the electrolyte membrane 30 is the same as that of the electrolyte membrane 10 shown in drawing 1, the explanation is omitted.

[0054]The anode 40a is provided with the following.

Diffusion zone 42a.

Catalyst bed 44a.

Hydrophobic layer 52a.

The cathode 40b is provided with the following.

Diffusion zone 42b.

Catalyst bed 44b.

Hydrophobic layer 52b.

[0055]The diffusion zone 42a is a layer for performing supply of the fuel gas to the catalyst bed 44a, and electronic transfer, and is provided in the gaseous phase side of the anode 40a. Similarly, the diffusion zone 42b is a layer for performing supply of the oxidant gas to the catalyst bed 44b, and electronic transfer, and is provided in the gaseous phase side of the cathode 40b. The construction material of the diffusion zones 42a and 42b has porosity and electron conductivity, and should not just be limited in particular. Generally, a porous carbon cloth, a carbonic paper, etc. are used.

[0056]The catalyst beds 44a and 44b are layers used as the reaction field of a cell reaction, and are provided in the field which touches the electrolyte membrane 20, respectively. The catalyst bed 44a of the anode 40a

is provided with the following.

Carrier 46a.

The catalyst 48a supported by the carrier 46a.

The electrolyte 50a in a catalyst bed.

Similarly, the catalyst bed 44b of the cathode 40b is provided with the following.

Carrier 46b.

The catalyst 48b supported by the carrier 46b.

The electrolyte 50b in a catalyst bed.

[0057]The construction material in particular of the carriers 46a and 46b and the catalysts 48a and 48b is not limited, and various construction material can be used for it according to a use. Generally, carbon is used for the carriers 46a and 46b, and Pt or a Pt alloy is used for the catalysts 48a and 48b. As shown in drawing 2, the catalysts 48a and 48b may be included in the catalyst beds 44a and 44b, after having been supported by the carriers 46a and 46b, but the catalysts 48a and 48b may be independently included in the catalyst beds 44a and 44b.

[0058]The electrolytes 50a and 50b in a catalyst bed are added, respectively in order to give ion conductivity to the catalyst beds 44a and 44b. The construction material in particular of the electrolytes 50a and 50b in a catalyst bed is not limited, and various construction material can be used for it according to a use. Usually, the solid polymer electrolyte of a fluorine system and the solid polymer electrolyte of a hydrocarbon system which are represented by the perfluorocarbon-sulfonic-acid system polymer are used. In order to form the hydrophobic layers 52a and 52b, the solid polymer electrolyte which has a canal segment in the end or side chain of a main chain may be used for the surface of the electrolytes 50a and 50b in a catalyst bed as the electrolytes 50a and 50b in a catalyst bed, respectively. This point is mentioned later.

[0059]The hydrophobic layers 52a and 52b are formed, respectively so that the gaseous phase side surface of the electrolytes 50a and 50b in a catalyst bed may be covered. If it has the hydrogen permeability which can supply the hydrogen contained in fuel gas to the catalyst bed 44a, and the water repellence which can control discharge of the water from the catalyst bed 44a to the diffusion zone 42a, the hydrophobic layer 52a by the side of the anode 40a. Even if it is which construction material, it can be used and is not limited in particular. However, in order to give CO-proof nature to the anode 40a, especially the fluorine system material that has C-F combination is suitable for the construction material of the hydrophobic layer 52a to intramolecular. If it has oxygen permeability and water repellence, even if the hydrophobic layer 52b by the side of the cathode 40b is which construction material, it can be used, and will not be limited in particular.

[0060]The thickness of the hydrophobic layers 52a and 52b can be arbitrarily chosen according to the construction material, as long as it has the reactant gas permeability and water repellence which are demanded. For example, as long as it has sufficient water repellence, the hydrophobic layers 52a and 52b may be monomolecular layers. As long as it, for example, has sufficient reactant gas permeability, the hydrophobic layers 52a and 52b may be high polymer layers which have predetermined thickness.

[0061]The area of the hydrophobic layers 52a and 52b is so good that it is large. It is because discharge of the water from the catalyst beds 44a and 44b to the diffusion zones 42a and 42b is controlled efficiently, so that the area of the hydrophobic layers 52a and 52b which cover the gaseous phase side surface of the

electrolytes 50a and 50b in a catalyst bed becomes large. However, in order to deliver and receive an electron between the catalyst beds 44a and 44b and the diffusion zones 42a and 42b, both need to be continuing electrically. Therefore, as for the hydrophobic layers 52a and 52b, it is preferred that the catalyst beds 48a and 48b or the carriers 46a and 46b are the layers which cover portions other than the portion in contact with the diffusion zones 42a and 42b and which continued substantially among the gaseous phase side surfaces of the catalyst beds 44a and 44b.

[0062]As such hydrophobic layers 52a and 52b, specifically, The polycondensation body layer obtained by carrying out the polycondensation of the hydrophobic metalaw KISAN precursor, The base layer obtained by carrying out the acid-base reaction of the ion exchange group and base in the gaseous phase side surface of the electrolytes 50a and 50b in a catalyst bed, the deposit layer which deposited a water-repellent material which has reactant gas permeability via the gaseous phase in the gaseous phase side surface of the electrolytes 50a and 50b in a catalyst bed, etc. are mentioned as a suitable example. Instead of the hydrophobic layers 52a and 52b forming a dissimilar material in the gaseous phase side surface of the electrolytes 50a and 50b in a catalyst bed, It may be a maldistribution layer obtained by making this canal segment unevenly distributed in the gaseous phase side surface of the catalyst beds 44a and 44b using the solid polymer electrolyte which the canal segment has combined with the end and side chain of a main chain as the electrolytes 50a and 50b in a catalyst bed.

[0063]The membrane electrode zygote 20 provided with the electrolyte membrane 30 by which the ion-conductive substance 34 was introduced in such a communicating hole 32a, and the catalyst beds 44a and 44b covered with the hydrophobic layers 52a and 52b, It is used in the state where it \*\*\*\*(ed) with the separator provided with the reactant gas channel for supplying reactant gas for the both sides like the conventional membrane electrode zygote.

[0064]Next, an operation of the fuel cell concerning this embodiment is explained. In drawing 2, if the fuel gas which contains hydrogen in the anode 40a side of the membrane electrode zygote 20 is supplied, hydrogen will arrive at the hydrophobic layer 52a surface through the diffusion zone 42a. Since the hydrophobic layer 52a has hydrogen permeability, diffusion of hydrogen is not checked, and hydrogen penetrates the hydrophobic layer 52a as it is, and reaches the catalyst 48b in the catalyst bed 44a.

[0065]In [ when using what has proton conductivity, respectively as the ion-conductive substance 34 and the electrolytes 50a and 50b in a catalyst bed ] the anode 40a, From hydrogen, a proton and an electron generate and move the generated proton to the cathode 40b via the ion-conductive substance 34 introduced in the electrolyte membrane 30. The generated electron is carried by load (not shown) from the diffusion zone 42a, and is further carried to the catalyst bed 44b through the diffusion zone 42b by the side of the cathode 40b from load.

[0066]On the other hand, if the oxidant gas which contains oxygen in the cathode 40b side is supplied, oxygen will arrive at the hydrophobic layer 52b surface through the diffusion zone 42b. Since the hydrophobic layer 52b has oxygen permeability, diffusion of oxygen is not checked, and oxygen penetrates the hydrophobic layer 52b as it is, and reaches the catalyst 48b in the catalyst bed 44b.

[0067]In the surface of the catalyst 48b, water generates from a proton, oxygen, and an electron. Since the hydrophobic layer 52b has high water repellence at this time, a part of moisture generated within the catalyst bed 44b stagnates in the catalyst bed 44b, without being discharged at the diffusion-zone 42b side. The

moisture which stagnated in the catalyst bed 44b is returned in the electrolyte membrane 30 by diffusion, and is reused by humidification of the electrolyte membrane 30.

[0068]Some water returned in the electrolyte membrane 30 is diffused in the anode 40a side. Since the gaseous phase side surface of the catalyst bed 44a by the side of [ 40a ] an anode is also covered with the hydrophobic layer 52a at this time, the moisture content discharged from the anode 40a side also decreases.

[0069]Since what introduced the ion-conductive substance 34 into the film base material 32 which has the communicating hole 32a penetrated to a thickness direction is used for the fuel cell concerning this embodiment as the electrolyte membrane 30 which constitutes the membrane electrode zygote 20, it can make ionic conductivity high, maintaining the intensity of the electrolyte membrane 30. Therefore, a fuel cell can be made high-powered and miniaturized.

[0070]Since the produced water by a cell reaction is reused by humidification of the electrolyte membrane 30, even if it does not supply water from the exterior using auxiliary machinery, it is maintained by the level which needs the water content of the electrolyte membrane 30 for a stable operation, and a high output is obtained by being stabilized.

[0071]When using reformed gas as fuel gas, a little CO gas may be contained in fuel gas. However, since the thin layer which consists of fluorine system material is [ the transmissivity of CO ] low, if this is used as the hydrophobic layer 52a by the side of the anode 40a, diffusion of CO to the catalyst bed 44a will be prevented. Therefore, poisoning of the catalyst 48a becomes is hard to be carried out by CO gas, and the endurance of an electrode improves.

[0072]Next, the example of the hydrophobic layers 52a and 52b is explained in detail. The 1st example of the hydrophobic layers 52a and 52b consists of a polycondensation body layer obtained by making the gaseous phase side surface of the catalyst beds 44a and 44b apply and carry out the polycondensation of the solution containing a hydrophobic metalaw KISAN precursor. Here, the hydrophobic metalaw KISAN precursor refers to the monomer or oligomer which produces metalaw KISAN combination by having a hydrophobic group and carrying out a polycondensation by a sol gel process. A hydrophobic metalaw KISAN monomer can be expressed with the formula of next \*\* 1. Hydrophobic metalaw KISAN oligomer means the amount object of 2 - 200 of a hydrophobic metalaw KISAN monomer expressed with the formula of \*\* 1.

[0073]

[Formula 1]  $X_{4-M[n]}(OR)_n$  [0074]In the formula of \*\* 1, n is an integer to 1-3. M is tetravalent metalloid element or metallic element, and is mentioned as an example with preferred silicon, titanium, zirconium, etc. OR is an alkoxy group. Specifically, a methoxy group, an ethoxy basis, a propoxy group, a butoxy group, etc. are mentioned as a suitable example.

[0075]At least one should just be a hydrophobic group X combined with the element M. Especially the thing to which at least one hydrogen combined with carbon in an alkyl group, a cycloalkyl group, an allyl group, an aryl group, etc. replaced fluoride as a hydrophobic group is preferred. Hydrophobic groups may be hydrophobic, strong hydrocarbon groups (for example, a phenyl group, an alkyl group, an allyl group, etc.). When two or more hydrophobic groups have combined with the element M, each hydrophobic group may be the same or may differ.



[0076]As such a hydrophobic metalaw KISAN precursor, Specifically Trimethoxysilane (3,3,3-trifluoropropyl), (Tridecafluoro-1,1,2,2-tetrahydro octyl) Triethoxysilane, triethoxysilane (heptadecafluoro-1,1,2,2-tetrahydro decyl), etc. are mentioned as an example with these preferred oligomer.

[0077]When applying to a gaseous phase side surface of the electrolytes 50a and 50b in a catalyst bed a solution containing a hydrophobic metalaw KISAN precursor, one kind of hydrophobic metalaw KISAN precursor may be contained in a solution, or two or more sorts of hydrophobic metalaw KISAN precursors may be contained in it. What is necessary is just to adjust suitably coverage of a kind of hydrophobic metalaw KISAN precursor and concentration, and a solution contained in a solution according to reactant gas permeability, water repellence, etc. which are required of polycondensation body layer thickness which it is going to form, and a polycondensation body layer.

[0078]It says that "spreading" covers uniformly a gaseous phase side surface of the electrolytes 50a and 50b in a catalyst bed with a solution in this invention, and, specifically, dropping, brush coating, a spray, steamy contact, etc. are mentioned as a suitable example. The polycondensation method of a hydrophobic metalaw KISAN precursor can use various methods, such as a method on which a method, acid, or alkali to heat is made to act, and is not limited in particular.

[0079]If an ion exchange group is exposed to a gaseous phase side surface of the electrolytes 50a and 50b in a catalyst bed, moisture will be easy to be discharged at the diffusion-zone 42a and b [ 42 ] side via this ion exchange group. On the other hand, if a gaseous phase side surface of the electrolytes 50a and 50b in a catalyst bed is covered with a polycondensation body layer of a hydrophobic metalaw KISAN precursor, discharge of water from the catalyst beds 44a and 44b to the diffusion zones 42a and 42b will be controlled. Since a hydrophobic layer can be formed selectively, discharge of water is efficiently controlled by water which exists in a portion which an ion exchange group which serves as an outlet of water especially easily exposed, and an ion exchange group's own catalysis. And since such a polycondensation body layer has reactant gas permeability, diffusion of reactant gas to the catalyst beds 44a and 44b is not checked. Therefore, a fuel cell which stabilizes and operates under a condition of not humidifying is obtained.

[0080]Next, the 2nd example is explained. The 2nd example of the hydrophobic layers 52a and 52b consists of a base layer obtained by carrying out the acid-base reaction of an ion exchange group and a base in a gaseous phase side surface of the electrolytes 50a and 50b in a catalyst bed. As a base made to react to an ion exchange group, quarternary ammonium salt expressed with a formula of next \*\* 2 is mentioned as a suitable example.

[0081]

[Formula 2](R<sub>4</sub>N) Y [0082]In the formula of \*\* 2, although R is generally an alkyl group, an allyl group, an aryl group, etc., in this invention, the structure in particular of R is not limited and various quarternary ammonium salt can be used for it. In order to give high water repellence to a base layer, especially the hydrophobic group that at least one hydrogen combined with carbon in an alkyl group, an allyl group, an aryl group, etc. which were mentioned above replaced by fluoride is preferred for R. Each R [ which is combined with a nitrogen atom ] may be the same, or it may differ. Y is negative ion and the kind in particular is not limited.

[0083]Specifically as such a base, dodecyl trimethylammonium chloride, distearyl dimethylbenzylammonium chloride, 3,3,3-trifluoro TORIPURO pill trimethylammonium chloride, etc. are mentioned as a suitable

example.

[0084]What is necessary is just to apply to a gaseous phase side surface of the catalyst beds 44a and 44b a solution containing a base, in order to carry out the acid-base reaction of an ion exchange group and a base in a gaseous phase side surface of the electrolytes 50a and 50b in a catalyst bed. In this case, what is necessary is just to adjust suitably a kind of base contained in a solution, concentration of a solution, coverage of a solution, etc. according to reactant gas permeability, water repellence, etc. which are required of a base layer.

[0085]If the acid-base reaction of an ion exchange group and a base in a gaseous phase side surface of the electrolytes 50a and 50b in a catalyst bed is carried out, an ion exchange group will be blocked by base and discharge of water from the catalyst beds 44a and 44b to the diffusion zones 42a and 42b will be controlled. If a base especially provided with a hydrophobic group is used, in addition to a block of an ion exchange group, high water repellence will be given to a base layer by hydrophobic group. And since such a base layer has reactant gas permeability, diffusion of reactant gas to the catalyst beds 44a and 44b is not checked. Of course, since it is only \*\*\*\*\* (ing) selectively only an ion exchange group in a gaseous phase side surface, proton conductivity which is an original role is enough maintained by internal ion exchange group.

[0086]Next, the 3rd example is explained. The 3rd example of the hydrophobic layers 52a and 52b consists of a deposit layer obtained by depositing a water-repellent material which has reactant gas permeability via the gaseous phase in a gaseous phase side surface of the electrolytes 50a and 50b in a catalyst bed. Specifically as a water-repellent material used for a deposit layer,  $CF_4$ , polytetrafluoroethylene (this is hereafter called "PTFE"), a fluoridation pitch, etc. are mentioned as a suitable example.

[0087]Various methods can be used for a method of carrying out a gaseous phase deposit according to a kind of water-repellent material to be used. For example, when using  $CF_4$  as a water-repellent material, a plasma treatment method is preferred. If plasma treatment using  $CF_4$  is performed to the surface of the electrolytes 50a and 50b in a catalyst bed, according to a processing condition, a carbon fluoride tunic of a multilayer can be formed in a gaseous phase side surface of the electrolytes 50a and 50b in a catalyst bed from a monomolecular layer.

[0088]Sputtering process is preferred when using PTFE as a water-repellent material for example. If sputtering processing of PTFE is performed to the surface of the electrolytes 50a and 50b in a catalyst bed, a PTFE tunic of arbitrary thickness can be formed in a gaseous phase side surface of the electrolytes 50a and 50b in a catalyst bed according to a processing condition.

[0089]When using a fluoridation pitch as a water-repellent material for example, a steamy contact process is preferred. If the electrolytes 50a and 50b in a catalyst bed are made to carry out steamy contact of the fluoridation pitch, a fluoridation pitch tunic of arbitrary thickness can be formed in a gaseous phase side surface of the electrolytes 50a and 50b in a catalyst bed according to a processing condition.

[0090]A water-repellent material of a fluorine system is difficult to form in a gaseous phase side surface of the electrolytes 50a and 50b in a catalyst bed a uniform tunic which consists of a water-repellent material by a method of applying a solution to a solvent, generally, since it is poorly soluble. On the other hand, according to a method of depositing via the gaseous phase, a uniform tunic can be formed along with micro unevenness of the electrolyte 50a in a catalyst bed, and 50b surface. And since a deposit layer obtained by

such a method has reactant gas permeability, diffusion of reactant gas to the catalyst beds 44a and 44b is not checked.

[0091]Next, the 4th example is explained. The 4th example of the hydrophobic layers 52a and 52b as the electrolytes 50a and 50b in a catalyst bed, It consists of a maldistribution layer obtained by making a canal segment unevenly distributed in a gaseous phase side surface of the electrolytes 50a and 50b in a catalyst bed using a solid polymer electrolyte (this is hereafter called "hydrophobic electrolyte".) which has a hydrophobic segment in an end and a side chain of a main chain.

[0092]Here, a canal segment means an atom group to whom it is expressed with general formula:  $\text{CF}_3-(\text{CF}_2)_n-$ . A canal segment may be straight chain shape, or even if there is branching on the way, it is not cared about. Generally, there is a tendency for the water repellence of a canal segment to become high, so that  $n$  becomes large. On the other hand, a value of  $n$  hardly affects reactant gas permeability. Therefore, a value of  $n$  can be arbitrarily chosen in consideration of water repellence, the manufacture ease of a hydrophobic electrolyte, etc. which are demanded. In order to give high water repellence to a maldistribution layer, two or more are desirable still more preferred, and  $n$  is ten or more. However, as for  $n$ , since solubility will fall and it will become difficult to form a catalyst bed if  $n$  exceeds 200, 200 or less are preferred.

[0093]Portions in particular other than a canal segment of a hydrophobic electrolyte are not limited. Namely, a hydrophobic electrolyte may combine a canal segment with an end and a side chain of a main chain of a solid polymer electrolyte with which all or a part of polymer skeleton was fluorinated, Or a canal segment may be combined with an end and a side chain of a main chain of a hydrocarbon system which do not contain fluoride. [ of a solid polymer electrolyte ]

[0094]Specifically as such a hydrophobic electrolyte, what combined a canal segment with an end and a side chain of a main chain of a perfluorocarbon-sulfonic-acid polymer is mentioned as a suitable example. A hydrophobic electrolyte may be independently used for the electrolytes 50a and 50b in a catalyst bed, or a mixture of a hydrophobic electrolyte and an electrolyte which does not have a canal segment may be used for them.

[0095]If mixed liquor of the electrolytes 50a and 50b in a catalyst bed containing a hydrophobic electrolyte and a catalyst supported to a catalyst or a carrier is applied to the surface of the electrolyte membrane 10 and a solvent is removed, the catalyst beds 44a and 44b will be formed. At this time, a solvent follows on being removed, a canal segment arranges to a gaseous phase side surface of the catalyst beds 44a and 44b, and a maldistribution layer is formed in a gaseous phase side surface of the electrolytes 50a and 50b in a catalyst bed. Thus, the obtained maldistribution layer can control discharge of water to the diffusion zones 42a and 42b, without checking diffusion of reactant gas to the catalyst beds 44a and 44b, since it has water repellence and moreover has reactant gas permeability.

[0096]Next, a manufacturing method of a fuel cell concerning this embodiment is explained. A fuel cell concerning this embodiment can be manufactured by various methods. First, the 1st manufacturing method joins the catalyst beds 44a and 44b to both sides of the electrolyte membrane 30 which introduced the ion conductivity substance 34 in the communicating hole 32a of the film base material 32, and ranks second to them, After forming the hydrophobic layers 52a and 52b in the surface of the electrolytes 50a and 50b in a catalyst bed uniformly using various methods mentioned above, it is the method of forming the diffusion

zones 42a and 42b in the surface of the catalyst beds 44a and 44b. In this case, the diffusion zones 42a and 42b are also good to join to the catalyst beds 44a and 44b, or to make it contact by conclusion at the time of cell attachment.

[0097]the catalyst bed 44a and the carriers 46a and 46b in 44b -- or, To a case in the state where the catalysts 48a and 48b were thoroughly covered by the electrolytes 50a and 50b in a catalyst bed. If junction or conclusion of the diffusion zones 42a and 42b is performed after forming the hydrophobic layers 52a and 52b in a gaseous phase side surface of the electrolytes 50a and 50b in a catalyst bed uniformly, A portion projected among the surfaces of the diffusion zones 42a and 42b breaks through the hydrophobic layers 52a and 52b and the electrolytes 50a and 50b in a catalyst bed, and it will be in the state where the catalyst beds 44a and 44b and the diffusion zones 42a and 42b were electrically open for free passage. If both sides of such a membrane electrode zygote 20 are \*\*\*\*(ed) with a separator provided with a reactant gas channel, a low temperature operation type fuel cell which operates stably also under conditions of not humidifying will be obtained.

[0098]First, the 2nd manufacturing method produces the sheet shaped catalyst beds 44a and 44b, and ranks second, Using various methods mentioned above, on the surface of the electrolytes 50a and 50b in a catalyst bed The hydrophobic layer 52a, After forming 52b uniformly, the hydrophobic layers 52a and 52b join the formed catalyst beds 44a and 44b to the electrolyte membrane 30, and are the methods of forming the diffusion zones 42a and 42b in the surface of the catalyst beds 44a and 44b further. It is also good to join the diffusion zones 42a and 42b also in this case, or to make it contact by conclusion. [0099]First, the 3rd manufacturing method forms the catalyst beds 44a and 44b in the surface of the electrolyte membrane 30, and ranks second to it, After forming the diffusion zones 42a and 42b in the surface of the catalyst beds 44a and 44b, It is the method of performing processing by being impregnated and a polycondensation of a hydrophobic metalaw KISAN precursor, and a base, a gaseous phase deposit of a water-repellent material, etc. from the diffusion-zone 42a andb [ 42 ] side, and forming the hydrophobic layers 52a and 52b in a gaseous phase side surface of the electrolytes 50a and 50b in a catalyst bed. Also by such a method, a low temperature operation type fuel cell which operates stably under conditions of not humidifying can be obtained.

[0100]After the 4th manufacturing method forms the catalyst beds 44a and 44b in the diffusion zones 42a and 42b, ranks second to them and forms the hydrophobic layers 52a and 52b in the surface of the electrolytes 50a and 50b in a catalyst bed from the diffusion-zone 42a andb [ 42 ] side first, it is the method of joining to the electrolyte membrane 30.

[0101]

[Example](Example 1) The electrolyte membrane concerning this invention was produced by the following procedures. The alumina membrane filter (Anodisc membrane filter made from Whatman) which a communicating hole 0.1 micrometer in diameter has penetrated at right angles to a field is used for a film base material at 43 mm in diameter, and 60 micrometers in thickness, The phenyltriethoxysilane sulfonic ester compounded by the known method was used for the ion conductivity substance.

[0102]First, the alumina membrane filter was immersed in the 1% ethanol solution of phenyltriethoxysilane sulfonic ester for 10 minutes at the room temperature, and it was air-dry at the room temperature.

Subsequently, this was heated at 110 \*\* for 10 minutes in the air, and phenyltriethoxysilane sulfonic ester



and the surface-water-of-aggregate acid radical in the communicating hole of an alumina membrane filter were combined by the coupling reaction. After cooling this to a room temperature, it rinsed lightly and the electrolyte membrane by which the ion conductivity substance of one molecular layer was introduced into the communicating hole internal surface was obtained.

[0103]The sulfonic group introduction amount was measured about the obtained electrolyte membrane. The sulfonic group introduction amount immersed the electrolyte membrane in the sodium chloride aqueous solution of 1M overnight, ranked second and asked for it by carrying out the neutralization titration of the solution in the sodium hydroxide solution of 0.05M.

[0104]Ionic conductivity was measured about the obtained electrolyte membrane. Ionic conductivity was measured by the exchange 2 terminal method with a frequency of 1 kHz. That is, the electrolyte membrane was pinched by Nafion 112 (made by Du Pont) of two sheets, the platinum board which plated platinum black from both sides was pressed by pressure 1.6MPa, resistance was measured, resistance of only Nafion 112 was deducted from this value, and it was considered as resistance of the electrolyte membrane.

[0105]For comparison, the sulfonic group introduction amount was similarly calculated by titration about Nafion 112 (made by Du Pont), and ionic conductivity was measured by the exchange 2 terminal method with a frequency of 1 kHz.

[0106]In the case of Nafion 112, the sulfonic group introduction amount per unit volume. (this is hereafter called "sulfonic group density".) -- it  $1.3\text{-mmol/cm}^{-3}(\text{ing})$  and, ionic conductivity was 0.08 S/cm and the ratio (this is hereafter called "specific conductance".) of ionic conductivity to sulfonic group density was  $0.062 (\text{S/cm})/(\text{mmol/cm}^3)$ .

[0107]On the other hand, in the case of the electrolyte membrane concerning this invention, sulfonic group density is  $0.158 \text{ mmol/cm}^3$ , ionic conductivity is 0.0182 S/cm, and it became a value lower than Nafion 112. However, specific conductance is  $0.12(\text{S/cm})/(\text{mmol/cm}^3)$ .

It became twice [ about ] Nafion 112.

According to the electrolyte membrane concerning this invention, this result shows that high ionic conductivity is obtained, even if it is when there are few sulfonic group introduction amounts relatively.

[0108]The polymer electrolyte membrane of a perfluorocarbon-sulfonic-acid system represented by Nafion is the sulfonic group density of number  $\text{mmol/cm}^3$ , and the distance between sulfonic groups is considered to be about 1 nm. the distance between sulfonic groups -- this -- short -- becoming (that is, equivalent weight is lowered) -- a film serves as water solubility in a certain place. Although ionic conductivity serves as the highest, the ionic conductivity beyond it stops then, coming out. It becomes difficult to maintain intensity, when a film serves as water solubility.

[0109]On the other hand, as for the electrolyte membrane concerning this invention, since intensity is maintained by a film base material, an ion exchange group introduction amount is not restricted for the above reasons. In the case of the electrolyte membrane obtained by this example, sulfonic group surface density is  $12.4/\text{nm}^2$ .

The value higher than a common polymer electrolyte is obtained.

[0110](Example 2) The fuel cell built over this invention by the following procedures was produced. First, the catalyst bed ( $13\text{-cm}^2$ ) which consists of carbon which made both sides of the electrolyte membrane concerning this invention obtained in Example 1 support a catalyst, and an electrolyte was joined. Subsequently, after the solution (fluorine solvent) of the trimethoxysilane (3,3,3-trifluoropropyl) of 300microl was uniformly dropped on the surface of the catalyst bed, the hydrophobic layer was formed on the surface of the catalyst bed by making it dry. Next, the diffusion zone was further joined to the outside of the catalyst bed, the both sides were further \*\*\*\*(ed) with the separator provided with the reactant gas channel, and the fuel cell was obtained.

[0111]The power generation examination was done using the obtained fuel cell. Power generation conditions were made into no two-poles humidifying, the cell temperature of  $100^\circ\text{C}$ , current density  $0.5\text{ A/cm}^2$ , the fuel excess rate 1.5, and the excess air factor 1.5 as fuel gas and oxidant gas using the reformed gas and air containing 10 ppm CO gas, respectively. Under no such elevated-temperature humidifying and the condition of high CO concentration, continuous running was possible for the fuel cell obtained by this example, it was stabilized and high power was obtained.

[0112]As mentioned above, although the embodiment of the invention was described in detail, various changes are possible for this invention within limits which are not limited to the above-mentioned embodiment at all, and do not deviate from the gist of this invention.

[0113]For example, although the hydrophobic layer is prepared for the both sides of the anode and the cathode, it may be made to provide a hydrophobic layer in either [ at least ] an anode or a cathode in the fuel cell shown in drawing 2. When using what has proton conductivity as an ion-conductive substance, since more water is discharged from the cathode side, generally a hydrophobic layer may be provided only in the cathode side in this case.

[0114]Although the above-mentioned embodiment, for example, mainly explained the example using what was provided with the cation exchange group as an ion-conductive substance, the thing provided with the anion exchange group may be used as an ion-conductive substance electrolyte.

[0115]

[Effect of the Invention]Since the electrolyte membrane concerning this invention is provided with the film base material which has a communicating hole penetrated to a thickness direction, and the ion-conductive substance introduced into the inside of said communicating hole, Even if it is when there are few introduction amounts of an ion-conductive substance, i.e., the introduction amount of an ion exchange group, relatively, it is effective in high ionic conductivity being obtained.

[0116]In this invention, the thing provided with the film base material which has a communicating hole penetrated to a thickness direction, and the ion-conductive substance introduced into the inside of said communicating hole is used as an electrolyte membrane in the fuel cell provided with the membrane electrode zygote to which the electrode was joined by both sides of the electrolyte membrane.

Therefore, it is effective in the ability to attain a high increase in power and miniaturization of a fuel cell.

[0117]Also in [ when it has a catalyst bed in which at least one side of an electrode contains the catalyst supported by the catalyst or the carrier and the electrolyte in a catalyst bed and the gaseous phase side

surface of the electrolyte in a catalyst bed is covered with the hydrophobic layer which has reactant gas permeability ] the bottom of the condition of not humidifying, The water content of an electrolyte membrane can be maintained to the level required for a stable operation, and it is effective in a high output being obtained by being stabilized.

[0118]As a hydrophobic layer, when fluorine system material is used, CO poisoning of the catalyst included in a catalyst bed is controlled, and it is effective in the endurance of an electrode improving.

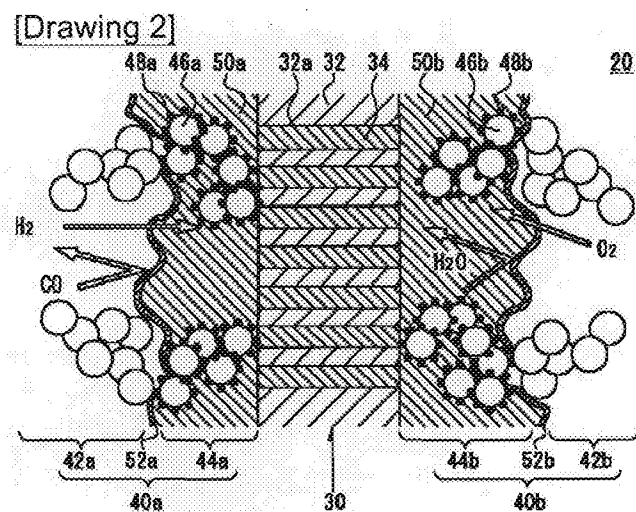
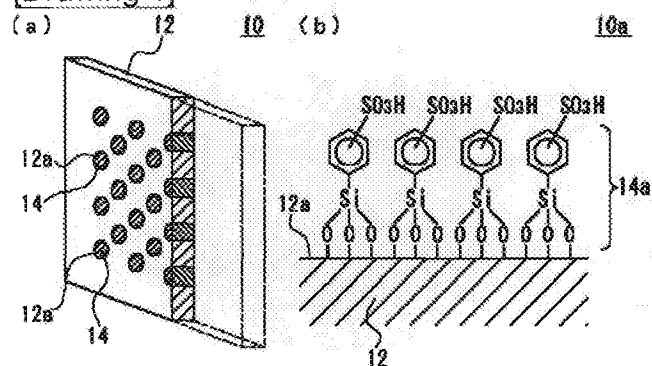
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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

[Drawing 1]



[Translation done.]